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THE OXIDATION OF FERROUS CHLORIDE: AN EXPLORATORY STUDY

by

E. Rolia* and B.J. Singbeil**

ABSTRACT

The oxidation of $FeCl_2$ with molecular oxygen has been examined in high ionic strength media of relevance to the regeneration of ferric chloride lixiviants used for leaching sulphide concentrates. In concentrated $FeCl_2$ solutions the reaction order for ferrous ion oxidation with respect to Fe^{2+} concentration is variable and decreases from second order to a lower order as the concentrations of Fe^{2+}, H^+ and Cl^- increase. For acid concentrations in the range 0.2-1.0 M HCl, the reaction order with respect to HCl is 0.29. Sodium chloride behaves as a catalyst and the rate of Fe^{2+} oxidation increases as 0.27 [NaCl]. The oxidation rate increases steadily with temperature to about 90°C, but appears to decrease at higher temperatures, possibly because of reduced oxygen solubilities. Over the temperature range 50-90°C, the average activation energy is 40.8 (standard deviation = 2.7) kJ mol^{-1}. There is a consensus that the iron oxidation rate is first order with respect to oxygen pressure.

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INTRODUCTION

The ferric ion leaching of base metal sulphides such as galena, sphalerite or chalcopyrite is being studied both to effect higher recoveries of the base metals and to recover sulphur in the elemental form. The ferric chloride leaching of galena concentrates is especially attractive because of the rapid dissolution rates and the facile production of a pure lead intermediate product, $PbCl_2$. Dutrizac and MacDonald (1) have reviewed ferric ion leaching in hydrometallurgical processes, and have cited the rapidity of lead concentrate dissolution. The recovery of lead from galena concentrates by ferric chloride leaching is currently being investigated by several groups (2,3,4). The stoichiometry of the leaching reaction is given by:

$$PbS + 2FeCl_3 \longrightarrow PbCl_2 + 2FeCl_2 + S^o \qquad (1)$$

In a commercial process, the ferric chloride lixiviant would be reduced, and an important subsequent operation would be the re-oxidation of the ferrous chloride reaction product so that it could be recycled within the process. The ferric chloride lixiviant used for leaching galena concentrates in a closed-loop process would be expected to contain high concentrations of iron, sodium chloride, zinc chloride and hydrochloric acid.

Several methods exist to effect the oxidation of $FeCl_2$ (1):

- electrolytic oxidation,
- use of chlorine gas,
- use of oxygen under pressure,
- use of oxygen at ambient pressure,
- use of strong oxidizers; e.g., H_2O_2, O_3,
- use of bacteria in the presence of oxygen.

The use of oxygen in air or as commercially pure oxygen is especially attractive for economic reasons. In the present work, oxygen at atmospheric pressure was employed to effect ferrous ion oxidation under approximated processing conditions.

The stoichiometry of the oxidation reaction is given by:

$$4Fe^{2+} + 4H^{+} + O_2 \longrightarrow 4Fe^{3+} + 2H_2O \qquad (2)$$

The equation shows that acid is consumed in a 1:1 molar ratio with respect to the iron oxidized. Over the last 100 years the kinetics of this oxidation reaction have been studied by numerous authors. The literature examined below shows that the mechanism is complex. Lowson (5) concludes that the kinetic order with respect to Fe^{2+} is a function of the media, pH, ferric ion concentration, oxygen concentration, temperature and catalyst (e.g., Cu^{2+}) concentration. In reporting kinetic results, therefore, it is necessary to define clearly all the operating conditions.

George (6) found that in perchloric acid media (0.005-1.0 N) over the temperature range 25-40°C the reaction was second order with respect to iron (0.025-0.23 M Fe^{2+}). Also the reaction was first order with respect to oxygen at atmospheric and higher oxygen pressures. The reaction constant increased slightly with decreasing H^{+} ion concentrations ($k \alpha [H^{+}]^{-0.23}$).

In 1 M H_2SO_4, Huffman and Davidson (7) found that the oxidation of ferrous ion (0.001-0.025 M Fe^{2+}) at 140-180°C proceeded by simultaneous bimolecular and termolocular reaction paths. The reaction rate was given by the equation:

$$\frac{-d[Fe^{2+}]}{dt} = k_b[Fe^{2+}]P_{O_2} + k_t[Fe^{2+}]^2P_{O_2} \qquad (3)$$

The hydrogen ion dependence of the reaction was uncertain but the reaction was found to be catalyzed by sulphate ions. The authors concluded from their own data and from a review of existing literature that the rate of oxidation in the presence of strong complexing agents such as phosphate or fluoride is first order with respect to Fe^{2+}. For the complexing agents of moderate strength, such as chloride or sulphate, the reaction is second order with respect to Fe^{2+}.

Iwai et al. (8) studied the oxidation of Fe^{2+} (0.2 M) in 0.1-3.0 M H_2SO_4 at temperatures ranging from 70 to 90°C. In solutions <0.4 M H_2SO_4 a decrease in H^+ ion concentration resulted in an increase in reaction rate. For solutions more acidic than 0.4 M H_2SO_4, the oxidation of Fe^{2+} proceeded through two parallel paths. In one, the reaction rate was proportional both to $[Fe^{2+}]^2$ and to the oxygen pressure (P_{O_2}), with an activation energy of 51.6 kJ mol^{-1}. In the other path, the reaction rate was proportional to $[Fe^{2+}]^2$, $[SO_4^{2-}]$ and P_{O_2} with an activation energy of 144.6 kJ mol^{-1}. In solutions containing 1.0-3.0 M H_2SO_4, the rate was independent of the hydrogen ion activity.

Posner (9) observed rapid oxidation of low concentrations of iron (0.055 M Fe^{2+}) in 4-8 M HCl solutions. The reaction was first order with respect to Fe^{2+} concentration and oxygen pressure, but a complex function of HCl concentration. The author proposed that the oxidation occurred by a mechanism with an intermediate complex formed between HCl and Fe^{2+} ions. Iwai et al. (10) observed first order oxidation kinetics with respect to Fe^{2+} in 3-6 M HCl. The authors proposed that an intermediate species, $HFeCl^{2+}$, combines with oxygen in the rate determining step.

Iwai and Majima (11) studied the oxidation of Fe^{2+} by molecular oxygen in spent pickle liquor containing hydrochloric acid. Second order reaction

kinetics with respect to Fe^{2+} were obtained in the range 1.4-2.0 M $FeCl_2$ and 0.5-2.2 M HCl. The authors concluded that the reaction rate depended on the concentration ratio of HCl to Fe^{2+}.

Iwai and Majima (12) also found that the oxidation reaction was 1.5 order with respect to Fe^{2+} for the oxidation of 0.7 M $FeCl_2$ in the acid concentration range 1.6-3.8 M HCl, but was first order in 4.4 M HCl. For solutions containing 1.4 M $FeCl_2$, the oxidation reaction was second order with respect to Fe^{2+} over the range 0.5-3.3 M HCl but order 1.5 at 3.8 M HCl.

Nikishova et al. (13) found that in a solution containing 1 M $FeCl_2$ and less than 2.32 M HCl the experimental data did not conform strictly to either first or second order rate equations. However, the data satisfy a second order kinetic equation which takes into account the loss of acid and the accumulation of ferric ions during the reaction.

To summarize, in hydrochloric acid solutions, the reaction order for ferrous oxidation, $\frac{-d[Fe^{2+}]}{dt} = k[Fe^{2+}]^n$, depends on both the ferrous ion concentration and the HCl concentration as given in Table 1.

Table 1 - Reported reaction orders for ferrous oxidation at various concentrations of $FeCl_2$ and HCl.

$[Fe^{2+}]$ (M)	[HCl] (M)	Order, n	Reference
0.055	4-8	1	(9)
0.2	3-6	1	(10)
0.7	4.4	1	(12)
0.7	1.6-3.8	1.5	(12)
1.4	3.8	1.5	(12)
1.4	0.5-3.3	2	(12)
1.4-2.0	0.5-2.2	2	(11)

It appears that first order oxidation kinetics with respect to Fe^{2+} are observed in solutions high in hydrochloric acid and low in $FeCl_2$; second order kinetics are observed in solutions low in hydrochloric acid and high in iron. There is a consensus that the rate of oxidation of $FeCl_2$ is directly proportional to the oxygen pressure; i.e., $\frac{-d[FeCl_2]}{dt} = k[Fe^{2+}]^n(P_{O_2})^{1.0}$.

EXPERIMENTAL

The current experiments were exploratory; i.e., designed to obtain background data on how reagent concentrations and temperatures influence the rate of $FeCl_2$ oxidation and to determine the reproducibility of the data. The oxidation of $FeCl_2$ was carried out in a 1.5 L glass reaction vessel enclosed in a water jacket; the solution was kept at a constant temperature by water supplied from a constant temperature water circulator. The reaction vessel was fitted with a removable titanium baffle with a split titanium ring. A propeller type titanium stirrer was driven at 1200 rpm by a Fisher dynamix stirrer. The high stirring rate and baffle provided excellent mixing of the liquid and gas phases.

Test solutions were prepared using reagent grade ferrous chloride ($FeCl_2.4H_2O$), hydrochloric acid (37%) and distilled water to give an experimental volume of 1.3 L. Oxygen gas (>99.9% O_2) was introduced into the solution through a fritted glass dispersion tube. Oxygen flow was maintained at 0.45 L min^{-1} and the reaction commenced with the start of the oxygen flow. At selected time intervals, 10-mL samples were withdrawn by pipette for chemical analysis. Total and ferrous iron were determined by titration with 0.1 N potassium dichromate using diphenylamine as the indicator. Free hydrochloric acid was determined by complexing hydrolyzable metal ions with MgEDTA reagent (14) and with titrating 0.1 N NaOH to a predetermined potentiometric end point at pH 6.3.

Three different experimental procedures were employed. In the first method, to explore the effect of reagent concentration, kinetic curves were obtained using both low and high concentrations of Fe^{2+}, H^{+} and Cl^{-} according to the plan:

$FeCl_2$		HCl		NaCl	
low	high	low	high	low	high
0.1 M	1.5 M	0.2 M	1.2 M	1 M	3 M

All tests were carried out at 85°C. Hydrochloric acid (12 M HCl) was added periodically from a burette to replace the acid consumed by Reaction 2, but this procedure was unable to keep the acid concentration constant during the experiments.

In the second procedure, the acid concentration was allowed to decrease as the oxidant reaction proceeded. After all the initial free acid had reacted, further acid was provided by the hydrolysis of ferric ions very much as would likely be done in a commercial operation where some iron precipitation would be desirable for iron control.

In the third procedure, the acid concentration was maintained approximately constant by the continuous addition of 12 M HCl to the reaction solution at a rate approximately equal to that at which the acid was consumed. The data from the first procedure were used to estimate the required flow rates. The rate of iron oxidation and the free acid concentration were checked by periodical sampling and analysis of the solution.

RESULTS AND DISCUSSION

PROCEDURE 1

High Iron Concentration

The effect of low and high concentrations of HCl and NaCl on the oxidation of 1.5 M $FeCl_2$ is shown in Figure 1. The kinetic curves indicate that the oxidation rate increased as either the HCl or NaCl concentrations increased. In the presence of high concentrations of both HCl and NaCl, the rate also increased, but not to the extent predicted from the additive sum of the individual oxidation curves. This indicates a mutually beneficial influence of HCl and NaCl on the oxidation rate of high concentrations of iron.

A semilogarithmic plot of the kinetic data from Figure 1 is shown in Figure 2. The linearity of the three upper curves indicates a first order dependence ($n = 1$) with respect to the Fe^{2+} concentration. The points of the lower curve are concave downward relative to the line joining the initial points, indicating $n < 1$. The results show that order with respect to Fe^{2+} in concentrated solutions depends on both the hydrogen ion and chloride ion concentrations. In the presence of high acid and high chloride concentrations, the order with respect to iron is less than one.

Low Iron Concentration

The effect of low and high concentrations of HCl and NaCl on the oxidation rate of 0.1 M $FeCl_2$ is shown in Figure 3. With all reactants at low concentration negligible oxidation of ferrous ion was detected in a 4-h period (upper curve). Oxidation occurred in the presence of high concentrations of either HCl or NaCl. The oxidation rate increased

dramatically in the presence of high concentrations of both HCl and NaCl (bottom curve). A semilogarithmic plot of these kinetic data is shown in Figure 4. In the presence of high concentrations of either acid or salt, the oxidation curve is slightly concave upward relative to the straight line joining the initial few points; thus, the reaction order with respect to Fe^{2+} is greater than unity. A linear relationship (n = 1) is observed in the presence of high concentrations of acid plus salt.

PROCEDURE 2

Effect of Acid Concentration in Concentrated $FeCl_2$ Solutions

The effect of different initial concentrations of hydrochloric acid on the oxidation rate of 1.5 M $FeCl_2$ is shown in Figure 5. The curves indicate that the oxidation rate is greater in the more concentrated acid solutions. In 3 M HCl (bottom curve) the reaction goes to 72% completion in 1 h; at 0.25 M HCl the reaction is only 25% complete in this period.

Figure 6, which summarizes the data of Figure 5, shows that the reaction is second order with respect to Fe^{2+} concentration in dilute acid media (0.25-1.6 M HCl) and order 1.5 in 3 M HCl.

Effect of Fe^{2+} Concentration in 3 M HCl Media

The effect of the initial ferrous ion concentration on the oxidation rate of Fe^{2+} in 3 M HCl media is shown in Figure 7. The same half-time for complete reaction (0.55 h) is observed for each curve. This result suggests that the reaction is first order with respect to ferrous ion concentration. Figure 6 shows the semilogarithmic plots of the kinetic data from Figure 7. The linear relationship, at least during the initial phases of reaction, confirms that the kinetics are first order with respect to the Fe^{2+} concentration.

Effect of Temperature

The effect of temperature on the rate of oxidation of Fe^{2+} in 1.5 M $FeCl_2$ and 1.5 M HCl media was determined and the kinetic curves obtained at the different temperatures are shown in Figure 9. A linear relationship for the inverse of ferrous ion concentration versus time (Figure 10) at the two boundary temperatures of 65°C and 95°C indicates that the second order reaction persists over the entire temperature range investigated.

PROCEDURE 3

Order with Respect to Ferrous Ion

The order of the oxidation reaction obtained in Procedure 2 is difficult to interpret because during the course of reaction there is a change in 3 variables: Fe^{2+} concentration, hydrochloric acid concentration and the extent of reaction. A more readily interpreted order with respect to Fe^{2+} is obtained if the hydrochloric acid is kept constant and only the initial rate of reaction is considered since there is less likelyhood of interference by the reaction products which may act as catalysts or inhibitors. In Procedure 3, the order of the oxidation reaction with respect to ferrous ion concentration was obtained from the slope of a double-logarithmic plot (15) of the initial rate of oxidation against the corresponding initial concentration of ferrous ion as determined in several independent experiments. The oxidation curves obtained in solutions with different initial concentrations of ferrous ion in 0.5 M HCl media are shown in Figure 11. The kinetic data were also plotted on a semilogarithmic basis, and the straight line joining the first few points of each plot was used to estimate the initial rate of oxidation and was also extended to obtain an estimated value for the reaction half-time ($t_{\frac{1}{2}}$). The results are given in Table 2.

Table 2 - Initial rates of oxidation for various concentrations of $FeCl_2$ in 0.5 M HCl at 85°C

Concentration $FeCl_2$ (M)	Estimated $t_{½}$ (s)	Rate x 10^5 (mol s^{-1})
0.5	26100	0.96
1.0	11520	4.3
1.5	6480	11.6
2.1	4320	23.1

Figure 12 shows the double-logarithmic plot of the initial rates of oxidation of Fe^{2+} against the corresponding initial concentrations of $FeCl_2$ in 0.5 M HCl media. A linear relationship is observed and the slope of the line is 2.2 (standard deviation = 0.04) which is the estimated reaction order with respect to ferrous ion. Within experimental error, the rate is probably second order with respect to the concentration of Fe^{2+}.

Order with Respect to Hydrochloric Acid

The kinetic curves for the oxidation of 1.5 M $FeCl_2$ media containing different low concentrations of hydrochloric acid ($[HCl] < [FeCl_2]$) are shown in Figure 13. During the experiments, the hydrochloric acid concentration was maintained nearly constant by the continuous addition of 12 M HCl at a rate approximately equal to that at which the acid was consumed by the reaction. The upper curve shows that oxidation can proceed without the addition of free acid, with the required acidity being supplied by the hydrolysis of the ferric ion reaction product.

$$Fe^{3+} + 2H_2O \longrightarrow \beta FeOOH + 3H^+ \qquad (4)$$

Figure 13 shows that oxidation rate increases as the free acid concentration increases.

The kinetic data from Figure 13 were plotted on a semilogarithmic basis and the initial rates were estimated from the straight line portions joining the first few points of each curve. The initial rates of oxidation of 1.5 M $FeCl_2$ at the different concentrations of free hydrochloric acid are given in Table 3.

Table 3 - Estimated initial rates of Fe^{2+} oxidation at different initial concentrations of free acid for 1.5 M $FeCl_2$ at 85°C and P_{O_2} 1 atm.

Concentration HCl (M)	Estimated $t_{\frac{1}{2}}$ (s)	Rate x 10^5 (mol s^{-1})
0.0	7920	9.5
0.2	7560	9.9
0.5	6300	11.9
1.0	4680	16.0

Figure 14 shows the double-logarithmic plot of the initial rate of Fe^{2+} oxidation against the initial concentration of free hydrochloric acid. The line is linear with a slope of 0.29 (standard deviation = 0.06) which is the estimated order for the oxidation of Fe^{2+} with respect to free acid in the range 0.2-1.0 M HCl. That is, $\frac{-d[Fe^{2+}]}{dt} = k[Fe^{2+}]^n[HCl]^{0.29}$. It should be noted at this time, however, that the error in the acid power dependence is large.

Effect of Temperature on the Oxidation Rate

The oxidation curves realized at various temperatures for an initial concentration of 1.5 M $FeCl_2$ and a constant 0.5 M HCl concentration are shown in Figure 15. The initial rates of oxidation were estimated from semilogarithmic plots of the kinetic data. A graph of the initial rate against temperature is shown in Figure 16. The reaction rate curve appears to drop rapidly above 90°C although this observation requires confirmation.

From the kinetic data of Figure 15, a pseudo-second order rate constant (k_2') was calculated using the integrated relationship for a second order rate reaction (13):

$$k_2' = \left(\frac{1}{C} - \frac{1}{Co}\right) \cdot \frac{1}{t} \qquad (5)$$

where Co is the initial concentration (mol L^{-1}) of $FeCl_2$ and C is the concentration at time t in seconds. For each 4-h run the rate constant values fluctuated around 10% of the average. An Arrhenius plot of k_2' is shown in Figure 17. Although there is some indication of two rate curves, the accuracy of these exploratory tests is such that the data are probably best fitted by a single curve whose slope yields an activation energy of 40.8 kJ mol^{-1} (standard deviation ±2.7 kJ mol^{-1}). It should be noted, however, that a recent Russian publication (17) also observed a falling off of the reaction rate at ∿90°C. This was attributed to a reduction in the oxygen solubility at high temperatures.

Effect of NaCl Concentration

Oxidation curves obtained in the presence of various concentrations of NaCl and for solutions initially containing 1.5 M $FeCl_2$ and 0.5 M HCl are shown in Figure 18. The kinetic data were plotted on a semilogarithmic

basis and typical results for 0.5 M NaCl and 2.8 M NaCl are shown in Figure 19. The results indicate a first order dependence of the Fe^{2+} oxidation rate on the ferrous ion concentration in sodium chloride solutions. A plot of pseudo-first order rate constants against the NaCl concentration is shown in Figure 20. The slope of the line is 0.27 (standard deviation = 0.05). The results indicate a slight catalytic effect of sodium chloride on the first order rate constant:

$$k_1' = 1.1 \times 10^{-4} + 0.27\,[NaCl]$$

SUMMARY

Preliminary tests (Figures 1-4) on the oxidation of Fe^{2+} by molecular oxygen showed that the reaction order with respect to ferrous ion concentration is a function of the concentrations of $FeCl_2$, HCl and NaCl. Increasing the concentration of any of these reagents to a high value lowered the reaction order with respect to ferrous ion, but increased the rate.

The results of the preliminary experiments in Figures 5-10 were difficult to interpret because both the ferrous and acid concentrations varied during the reaction. The decrease from second order to order 1.5 reaction in more concentrated acid solutions noted in Figure 6 suggests activation by free hydrochloric acid. The first order kinetics with respect to Fe^{2+} noted in Figures 7 and 8 are considered by some authors (7,10) to be the true order for Fe^{2+}. However, this interpretation is not conclusive because the H^+ ion concentration was not kept constant in those previous works. The true order with respect to ferrous ion is found only when ferrous ion alone is varied during oxidation. Figure 10 illustrates that there is no change in the reaction order with respect to Fe^{2+} when the temperature increases from 65°C to 95°C.

The effect of temperature on the oxidation rate suggests either that there is a significant decrease in the concentration of dissolved oxygen above 90°C or that there are two or more simultaneous oxidation paths with different activation energies. The average activation energy value 40.8 (standard deviation 2.7) kJ mol^{-1} over the temperature range 50-90°C is less than the reported values 51.6 kJ mol^{-1} (5) and 51.5 kJ mol^{-1} (8).

Figures 19 and 20 indicate that sodium chloride behaves as a catalyst with the oxidation rate increasing directly as 0.27[NaCl].

Additional studies are planned to complete the work initiated in this preliminary investigation. A better experimental method will be devised to keep the acid concentration constant during the reaction. Data are required at higher temperatures, elevated oxygen pressures and at still higher concentrations of the various reactants. The effects of high concentrations of the reaction products (e.g., $FeCl_3$) and of interfering substances will also be studied.

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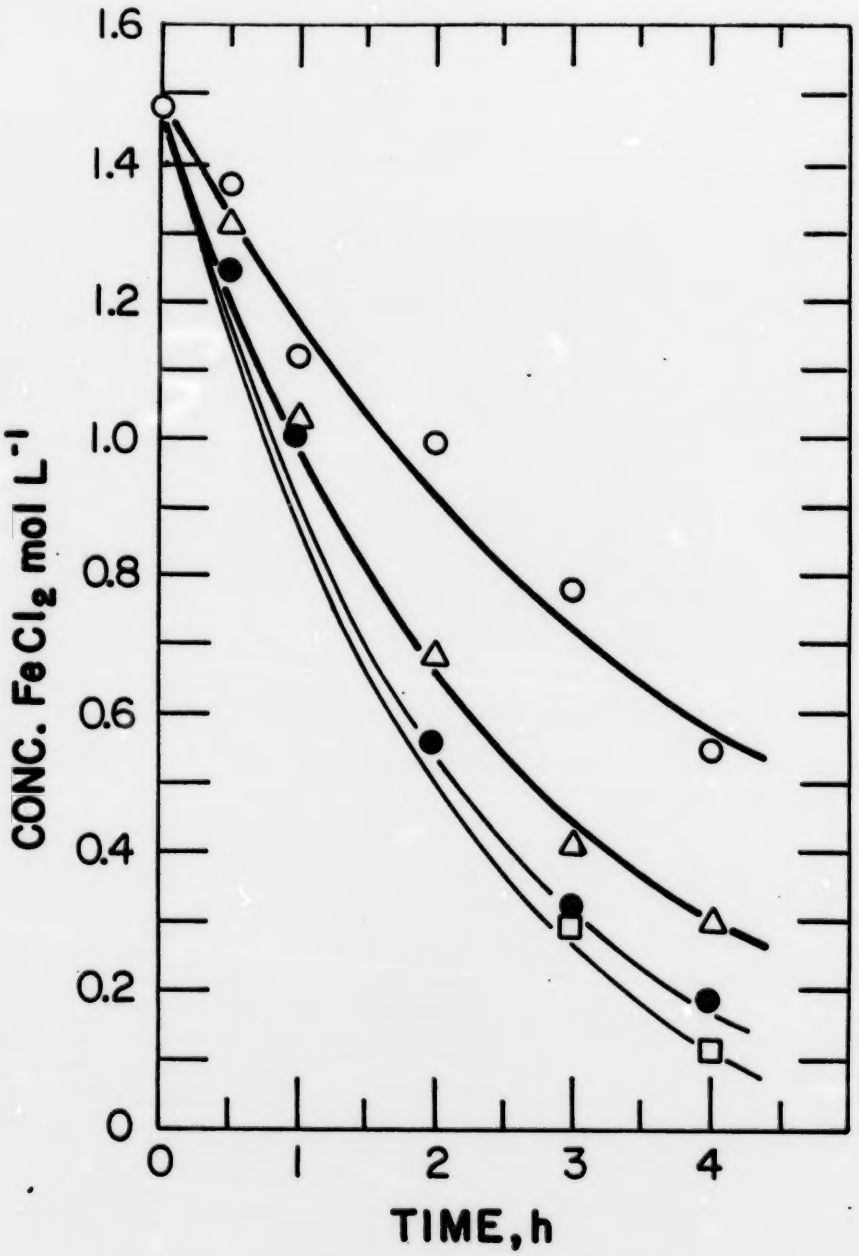

Fig. 1 - Effect of low and high concentrations of HCl and NaCl on the oxidation of 1.5 M $FeCl_2$ at 85°C and 1 atm oxygen pressure.

○ HCl 0.2 M, NaCl 1 M; △ HCl 0.2 M, NaCl 3 M;
● HCl 1.2 M, NaCl 1 M; □ HCl 1.2 M, NaCl 3 M.

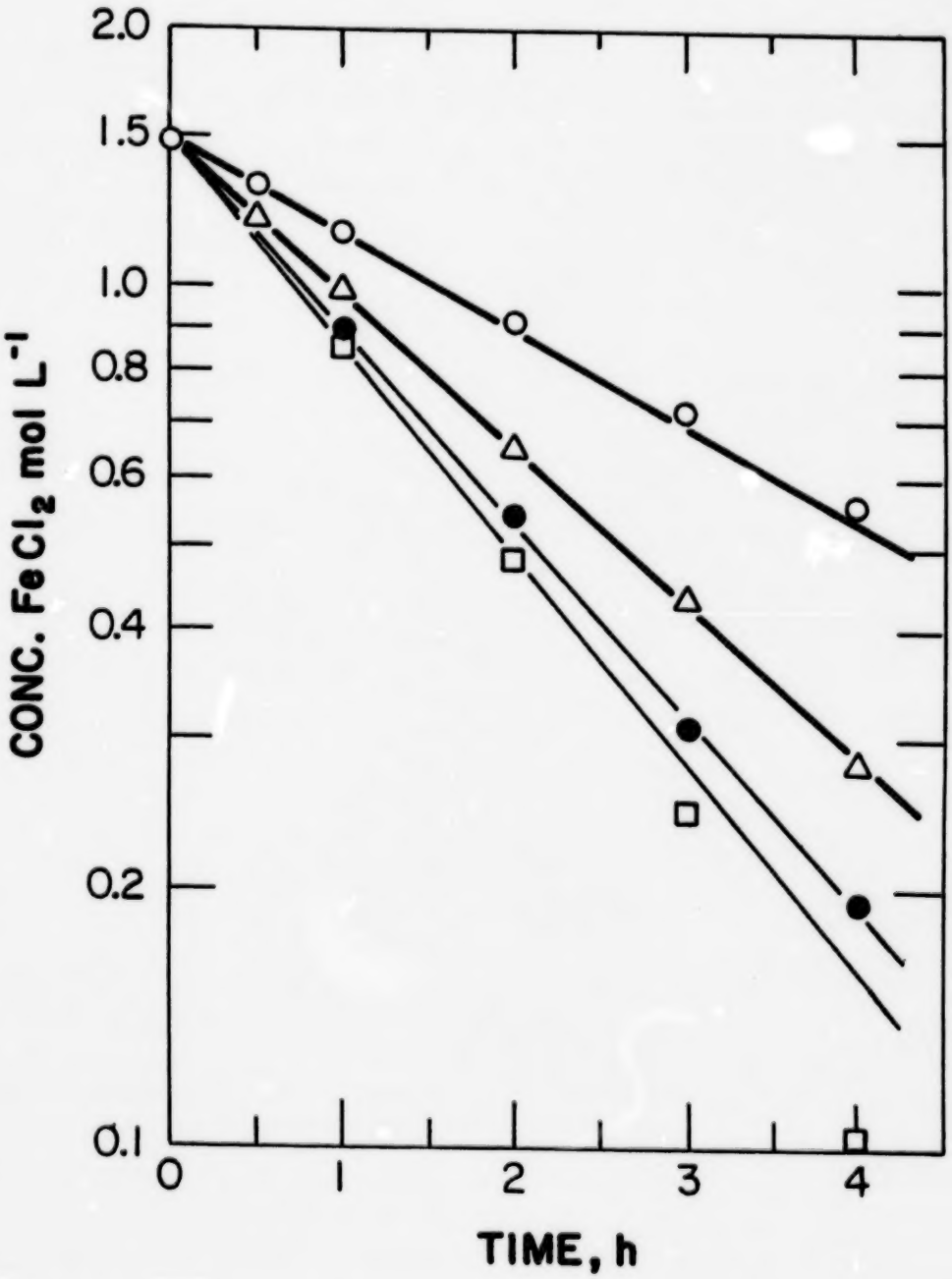

Fig. 2 - Semilogarithmic plot of the kinetic data of Figure 1.

○ HCl 0.2 M, NaCl 1 M; △ HCl 0.2 M, NaCl 3 M;
● HCl 1.2 M, NaCl 1 M; □ HCl 1.2 M, NaCl 3 M.

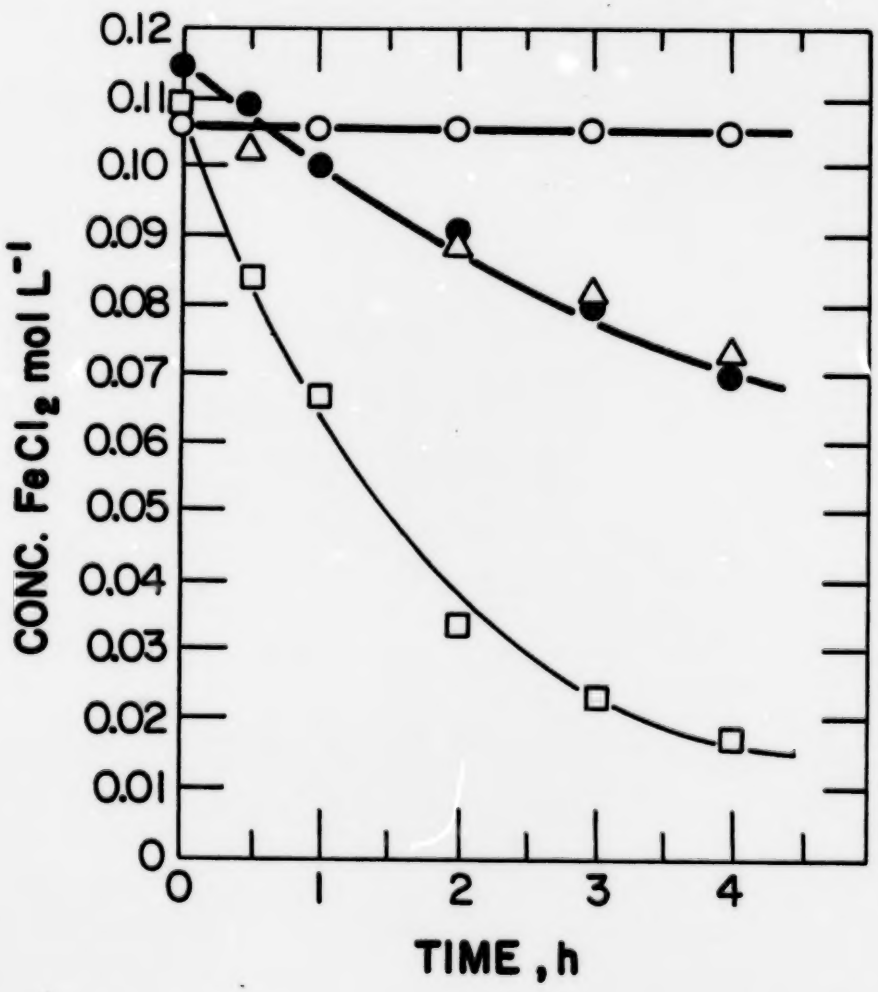

Fig. 3 - Effect of low and high concentrations of HCl and NaCl on the oxidation of 0.1 M $FeCl_2$ at 85°C and 1 atm oxygen pressure.

○ HCl 0.2 M, NaCl 1 M; △ HCl 1.2 M, NaCl 1 M;
● HCl 0.2 M, NaCl 3 M; □ HCl 1.2 M, NaCl 3 M.

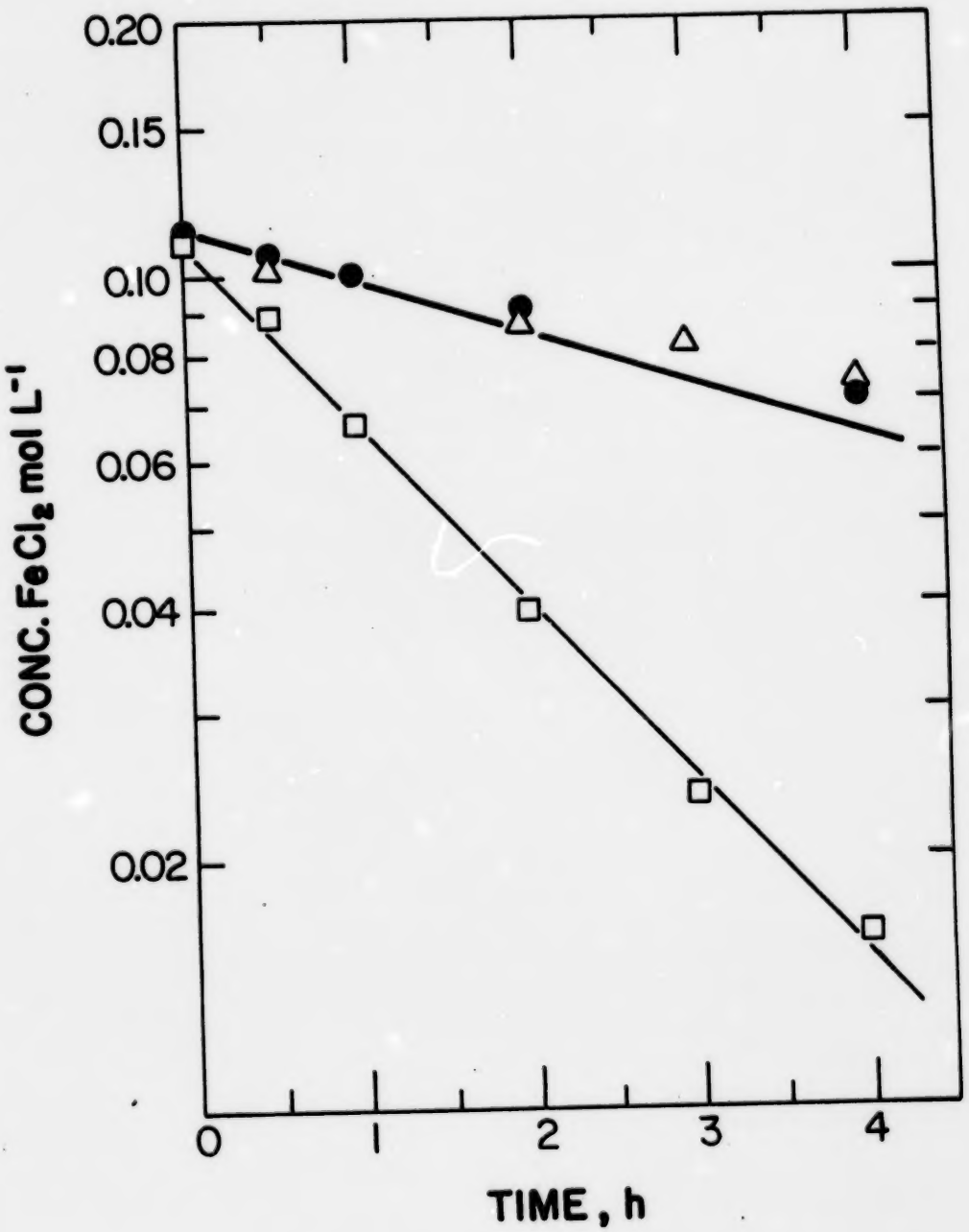

Fig. 4 - Semilogarithmic plot of the kinetic data of Figure 3.

● HCl 0.2 M, NaCl 3 M; ▲ HCl 1.2 M, NaCl 1 M;
□ HCl 1.2 M, NaCl 3 M.

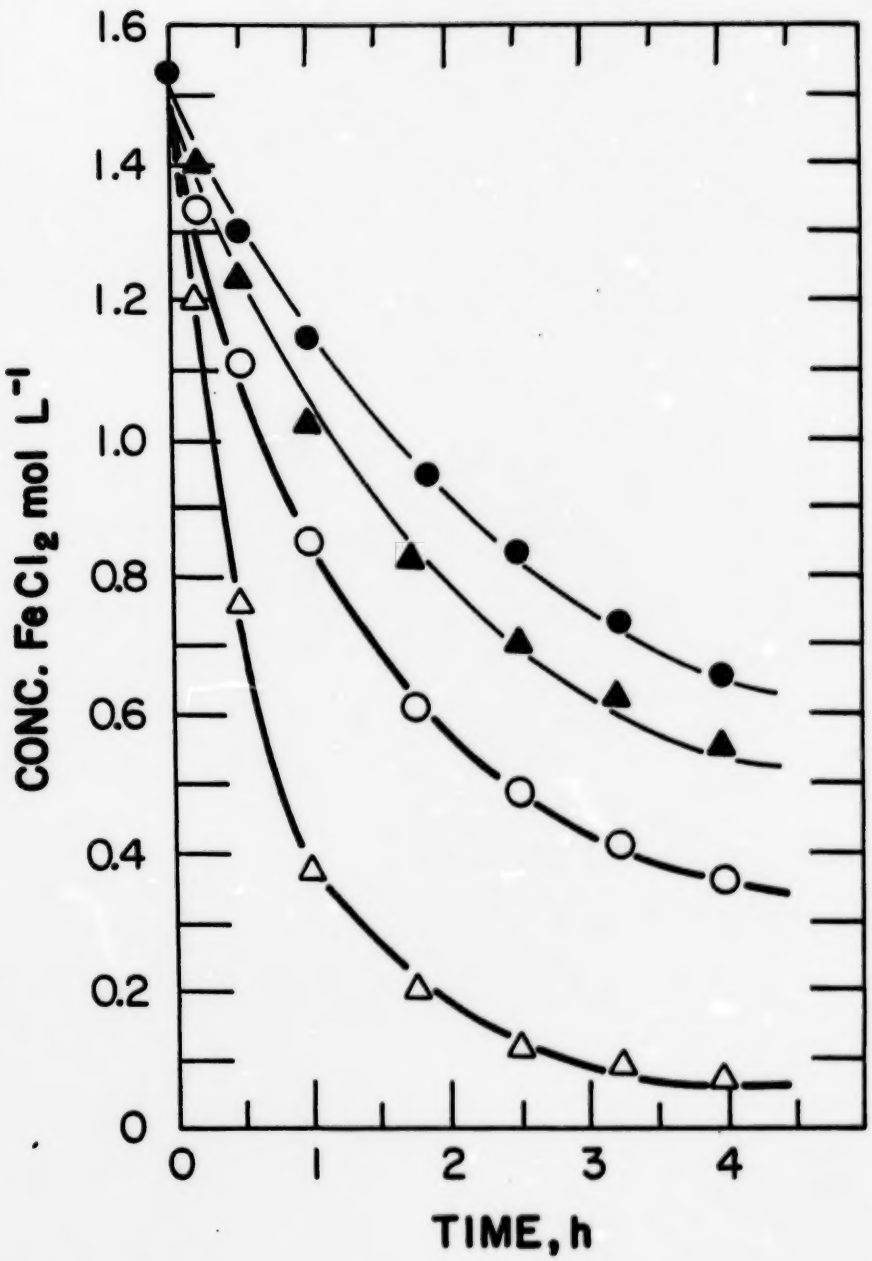

Fig. 5 - Effect of initial HCl concentration on the oxidation rate of 1.5 M $FeCl_2$ at 85°C and 1 atm oxygen pressure.

● HCl 0.25 M; ▲ HCl 0.785 M;
○ HCl 1.66 M; △ HCl 3.0 M.

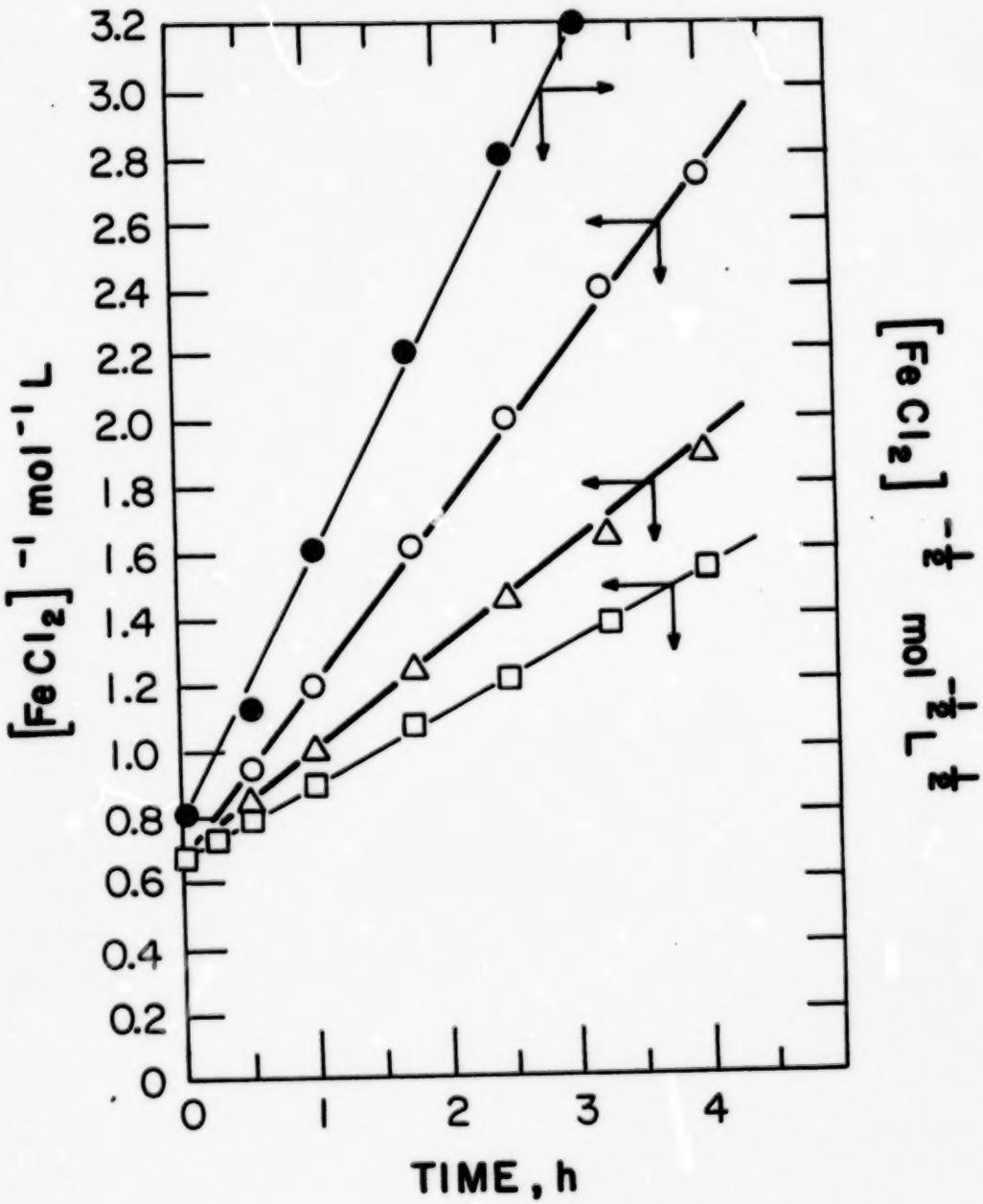

Fig. 6 - Plots of the kinetic data from Figure 5 that indicate second and 1.5 order relationships with respect to $FeCl_2$ concentration.

□ HCl 0.25 M; △ HCl 0.785 M;
○ HCl 1.66 M; ● HCl 3.0 M.

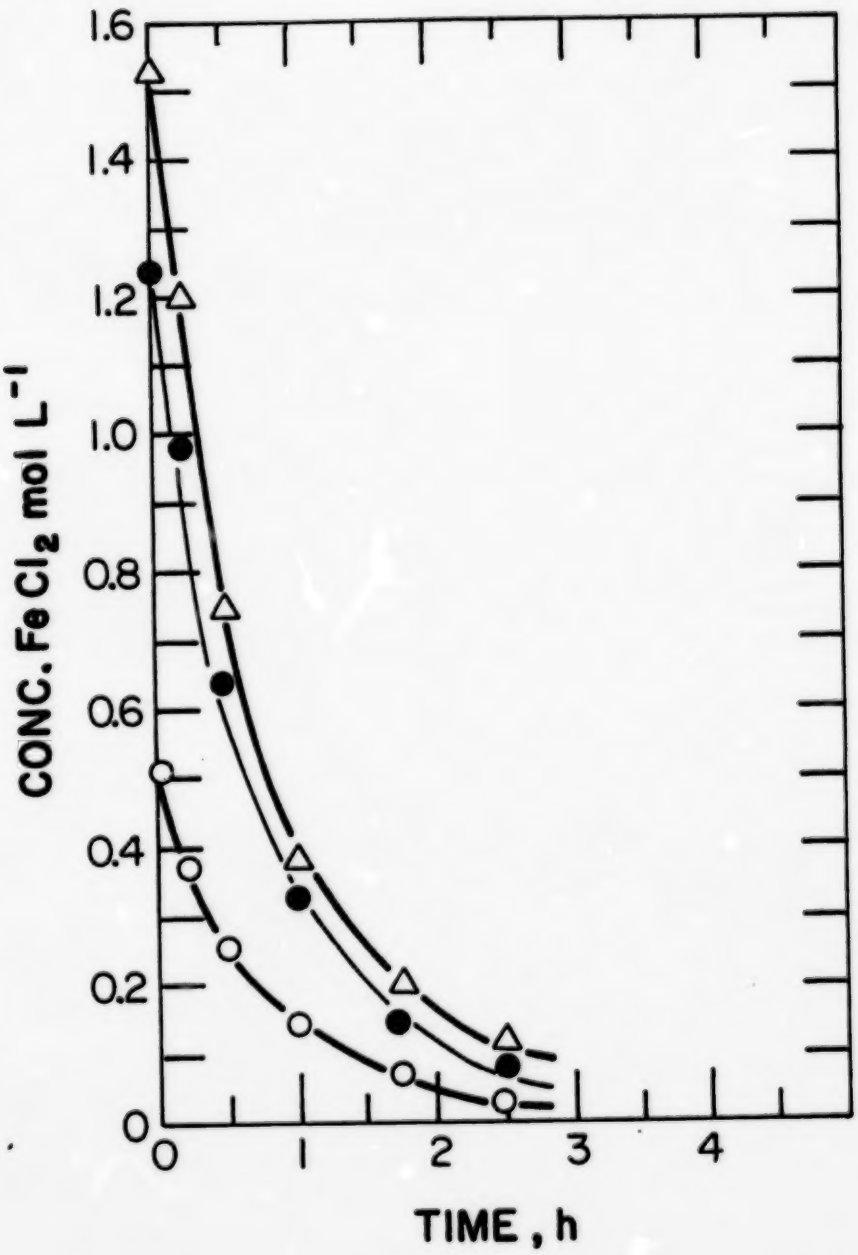

Fig. 7 - Effect of $FeCl_2$ concentration on the rate of oxidation in 3 M HCl and 85°C and 1 atm oxygen pressure.

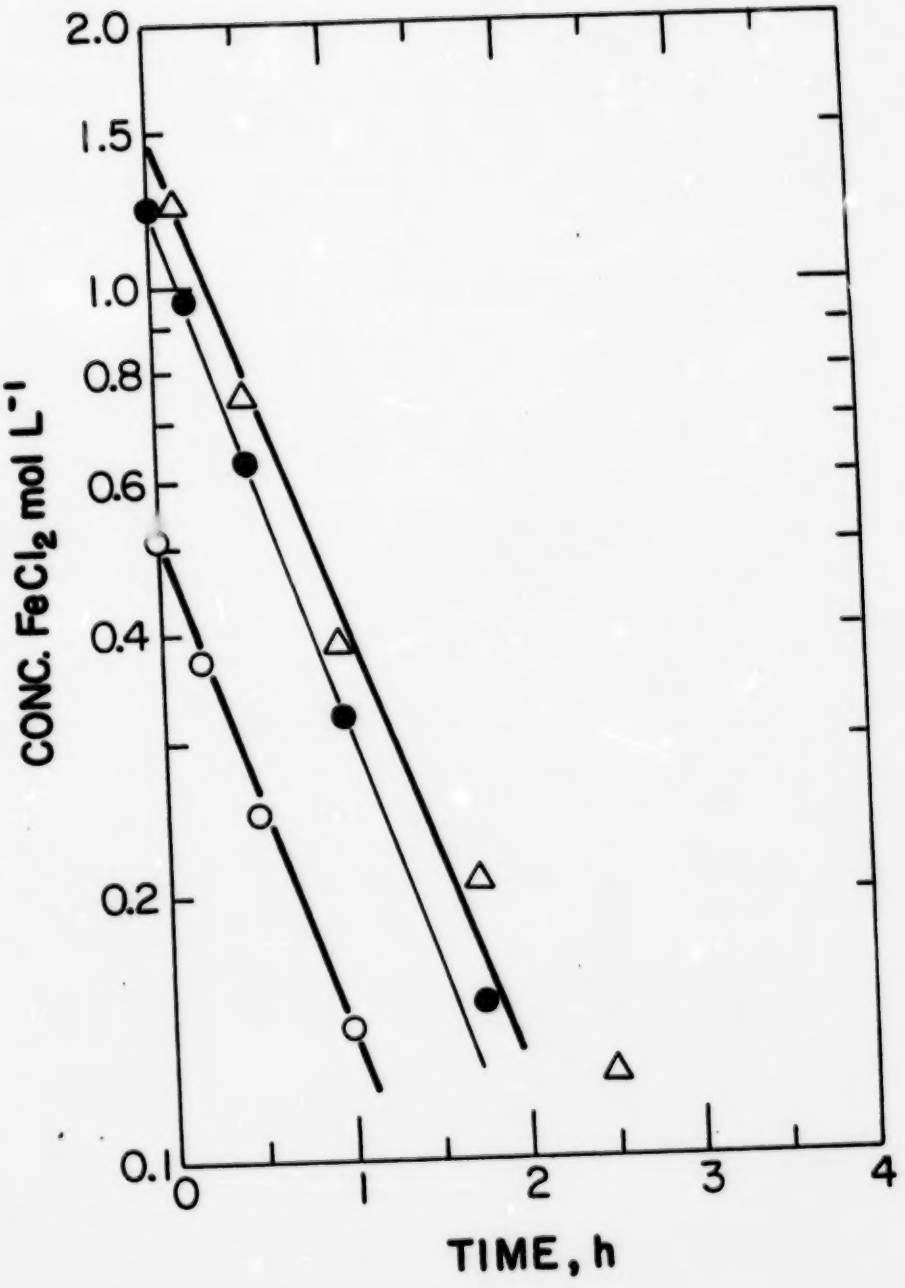

Fig. 8 - Semilogarithmic plots of the kinetic data of Figure 7 showing first order relationships.

Fig. 8

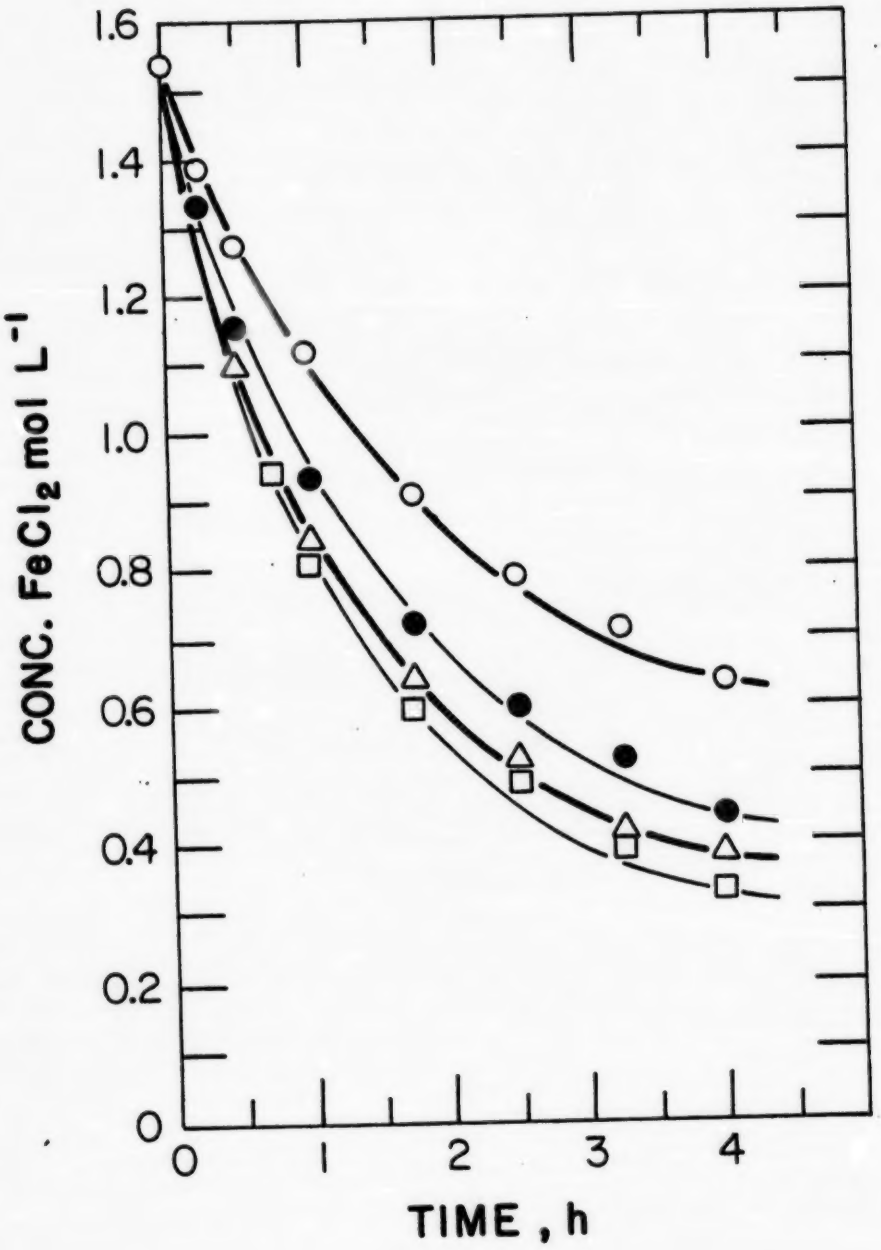

Fig. 9 - Effect of temperature on the rate of Fe^{2+} oxidation in 1.5 M $FeCl_2$ and 1.5 M HCl media at 1 atm oxygen pressure.

○ 65°C; ● 75°C; △ 85°C; □ 95°C

Fg .9.

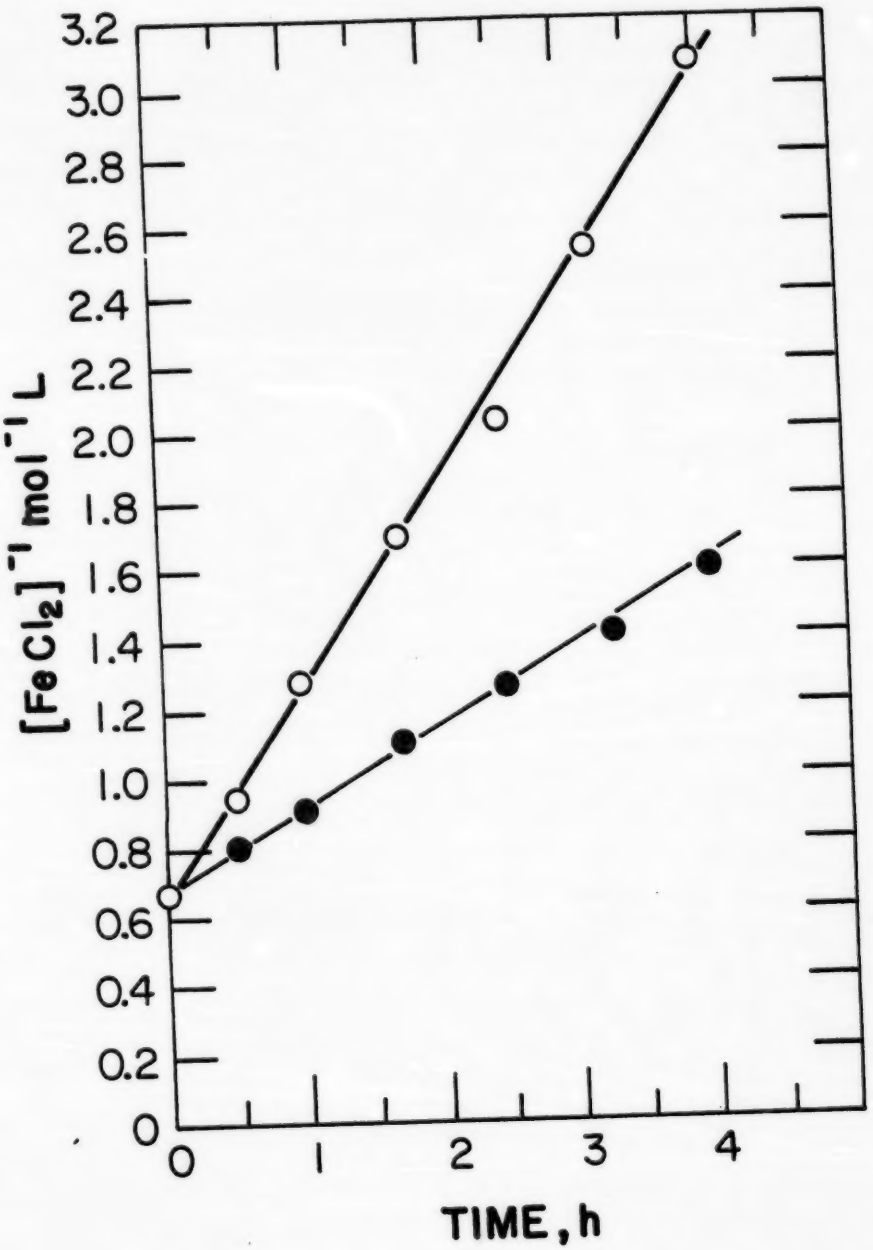

Fig. 10 - Plots of the kinetic data from Figure 9 showing a second order relationship for the boundary temperatures of 65° and 95°C.

● 65°C; ○ 95°C

Fig. 10.

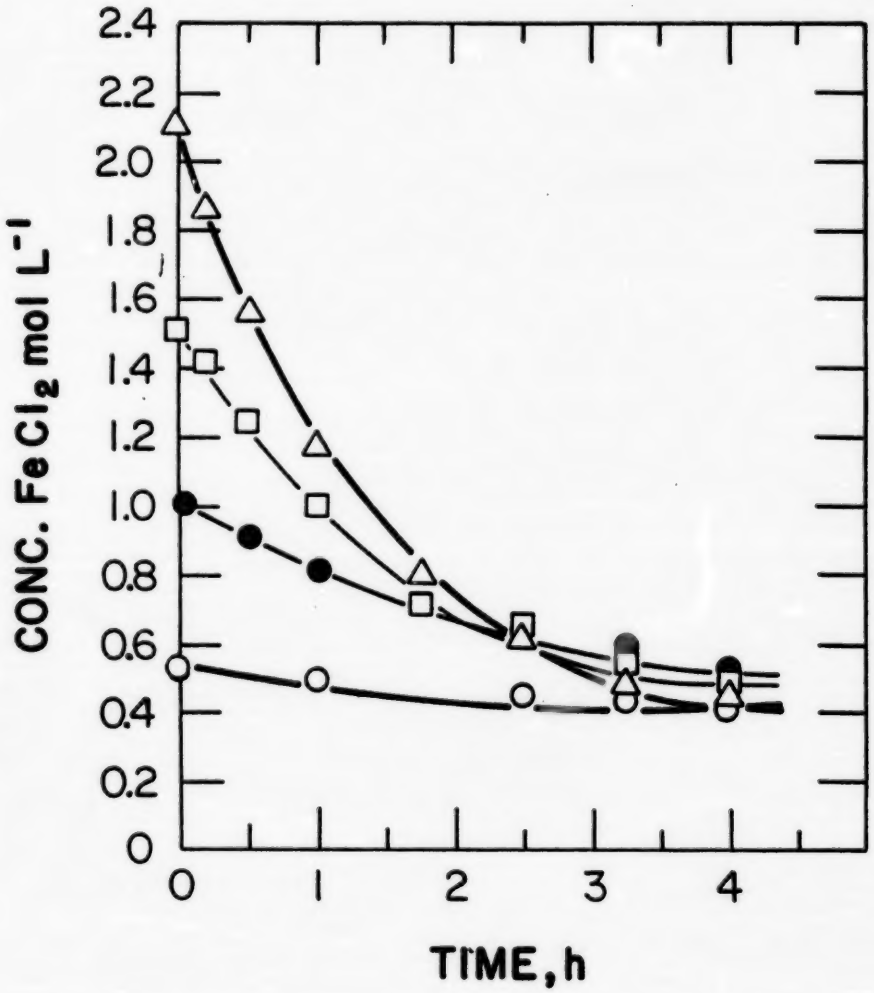

Fig. 11 - Effect of ferrous concentration on the rate of Fe^{2+} oxidation in 0.5 M HCl media at 85°C and 1 atm oxygen pressure.

Fig. 11.

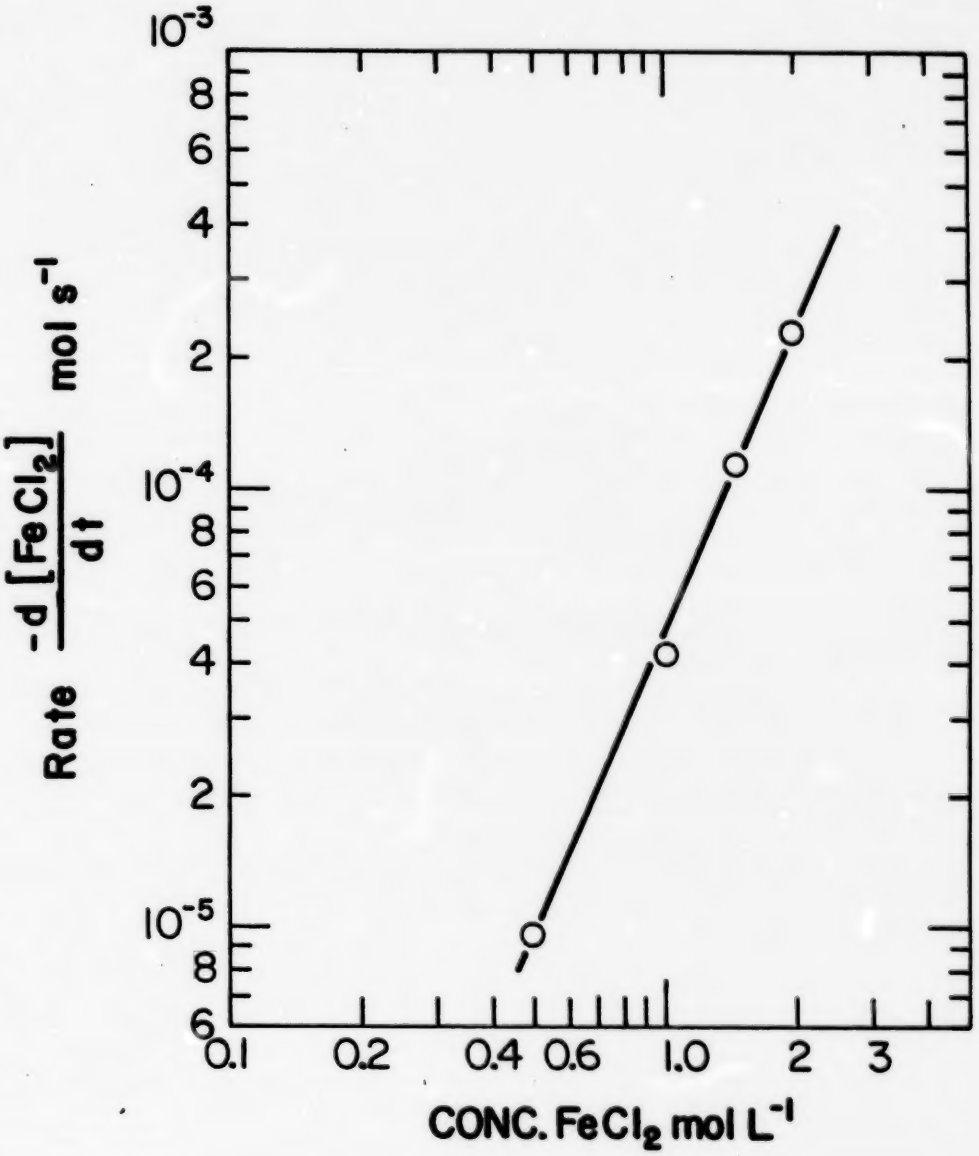

Fig. 12 - The logarithm of the initial rates of oxidation versus the logarithm of the initial concentrations of Fe^{2+}.

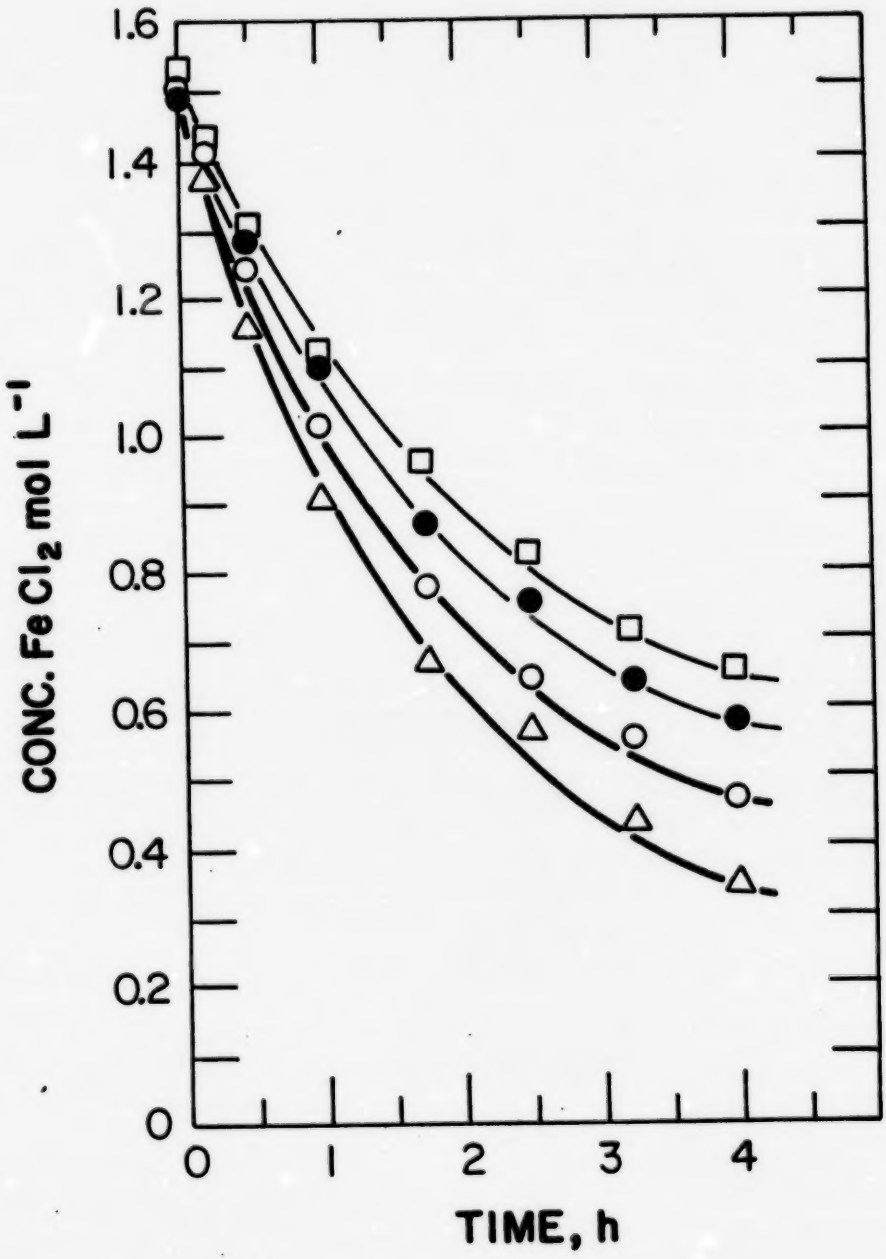

Fig. 13 - Oxidation curves realized when the initial acid concentration was maintained constant; solutions contained 1.5 M $FeCl_2$ at 85°C and 1 atm oxygen pressure.

□ HCl nil; ● HCl 0.2 M; ○ HCl 0.5 M; △ HCl 1.0 M

Fig. 13.

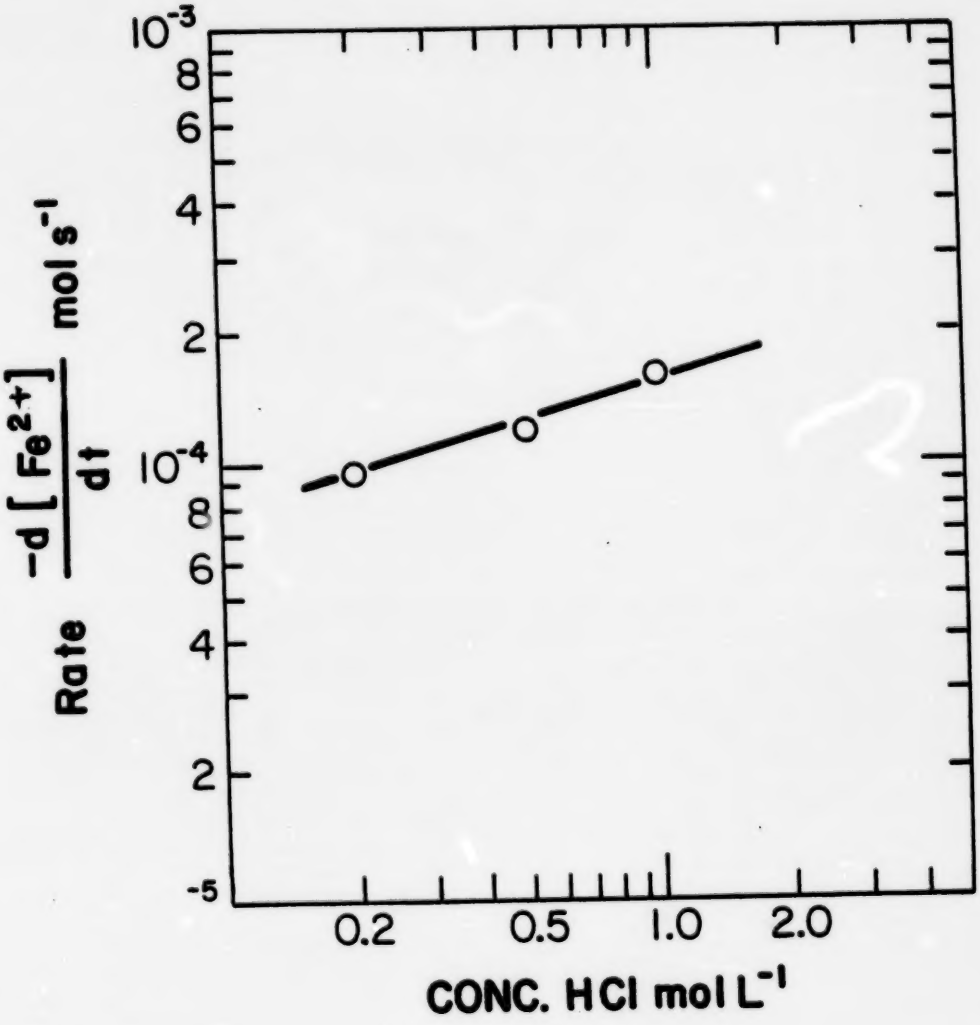

Fig. 14 - The logarithms of the initial rates of oxidation versus the logarithms of the concentrations of HCl.

Fig. 14

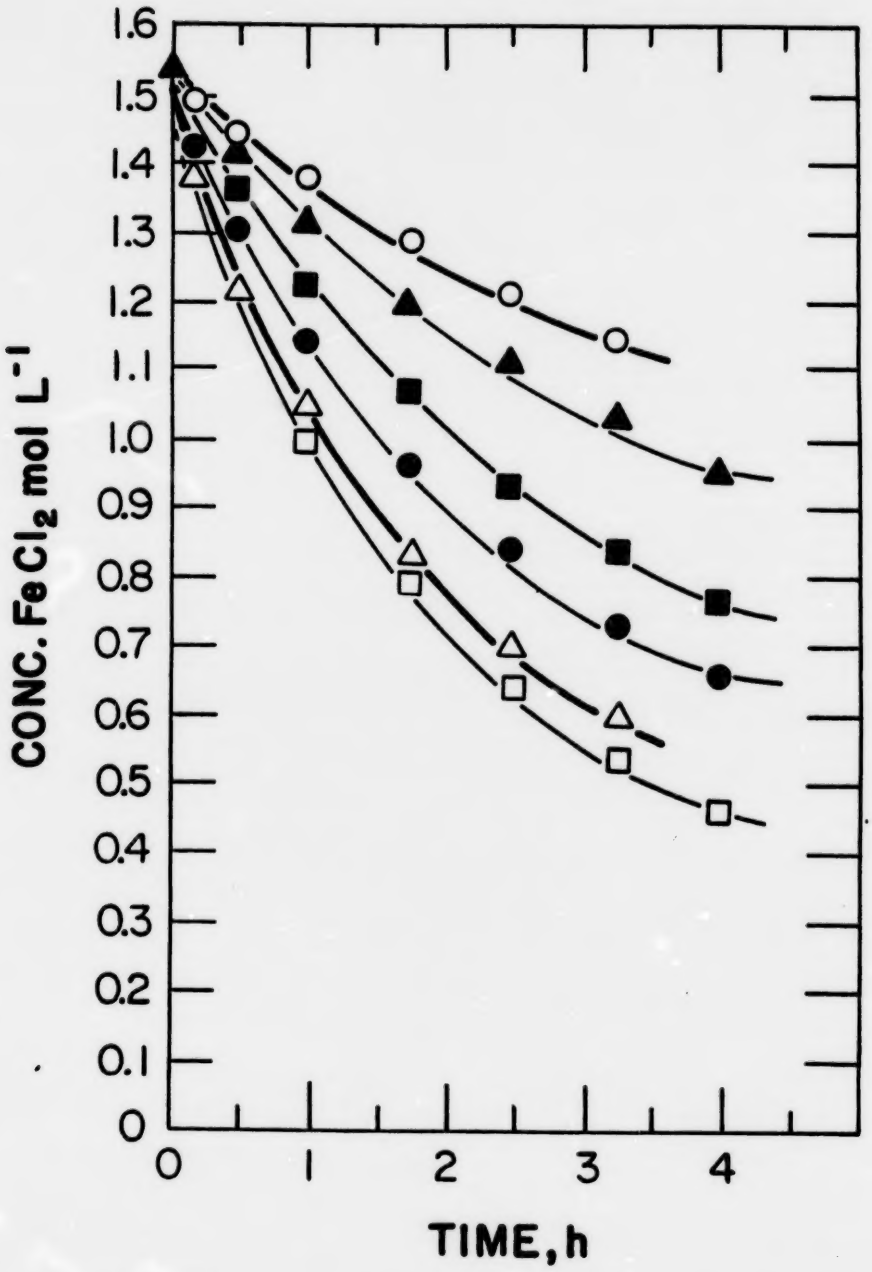

Fig. 15 - Oxidation curves realized at various temperatures for solutions containing 1.5 M $FeCl_2$ in 0.5 M HCl at 1 atm oxygen pressure.

○ 50°C; ▲ 56°C; ■ 65°C; ● 70°C; △ 80°C; □ 90°C

Fig. 15

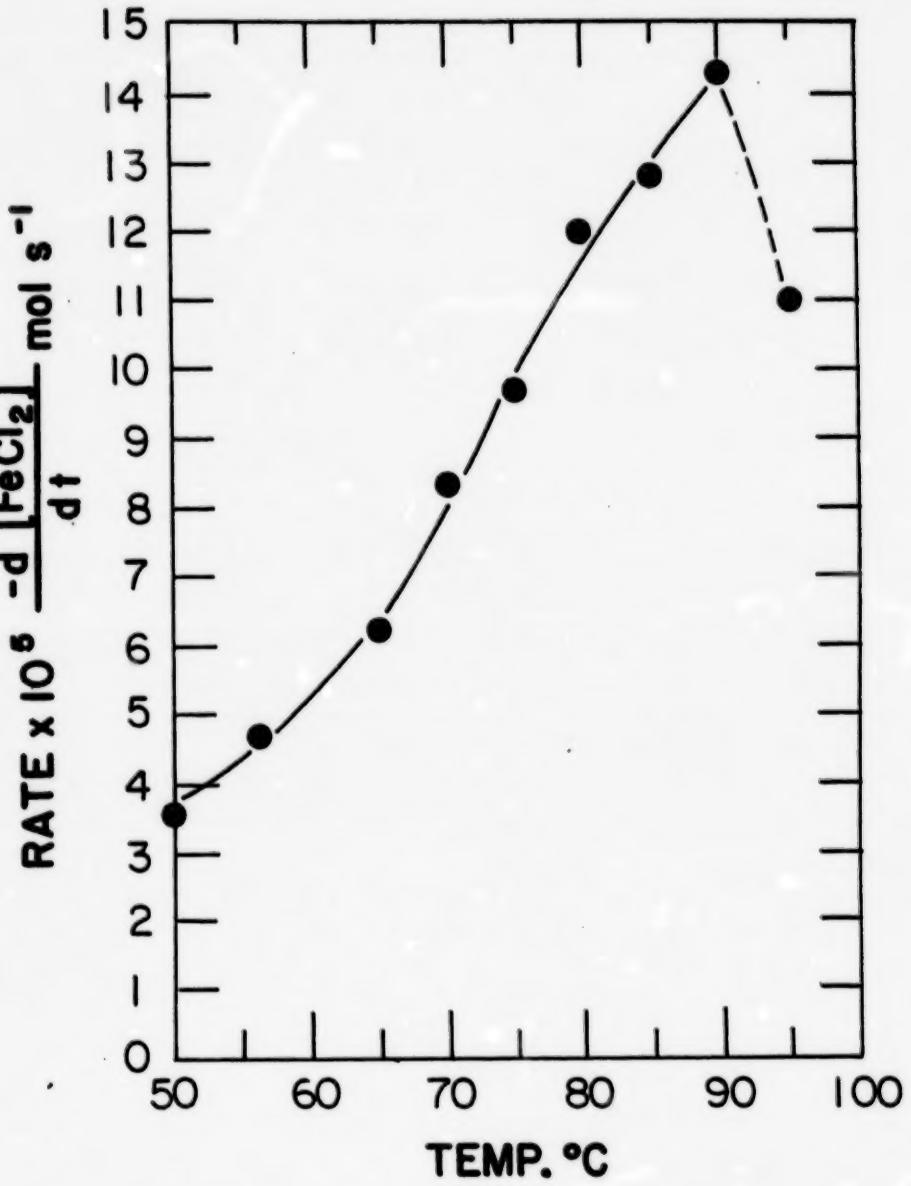

Fig. 16 - Plot of initial oxidation rate of a 1.5 M $FeCl_2$ - 0.5 M HCl solution against temperature (°C) at 1 atm oxygen pressure.

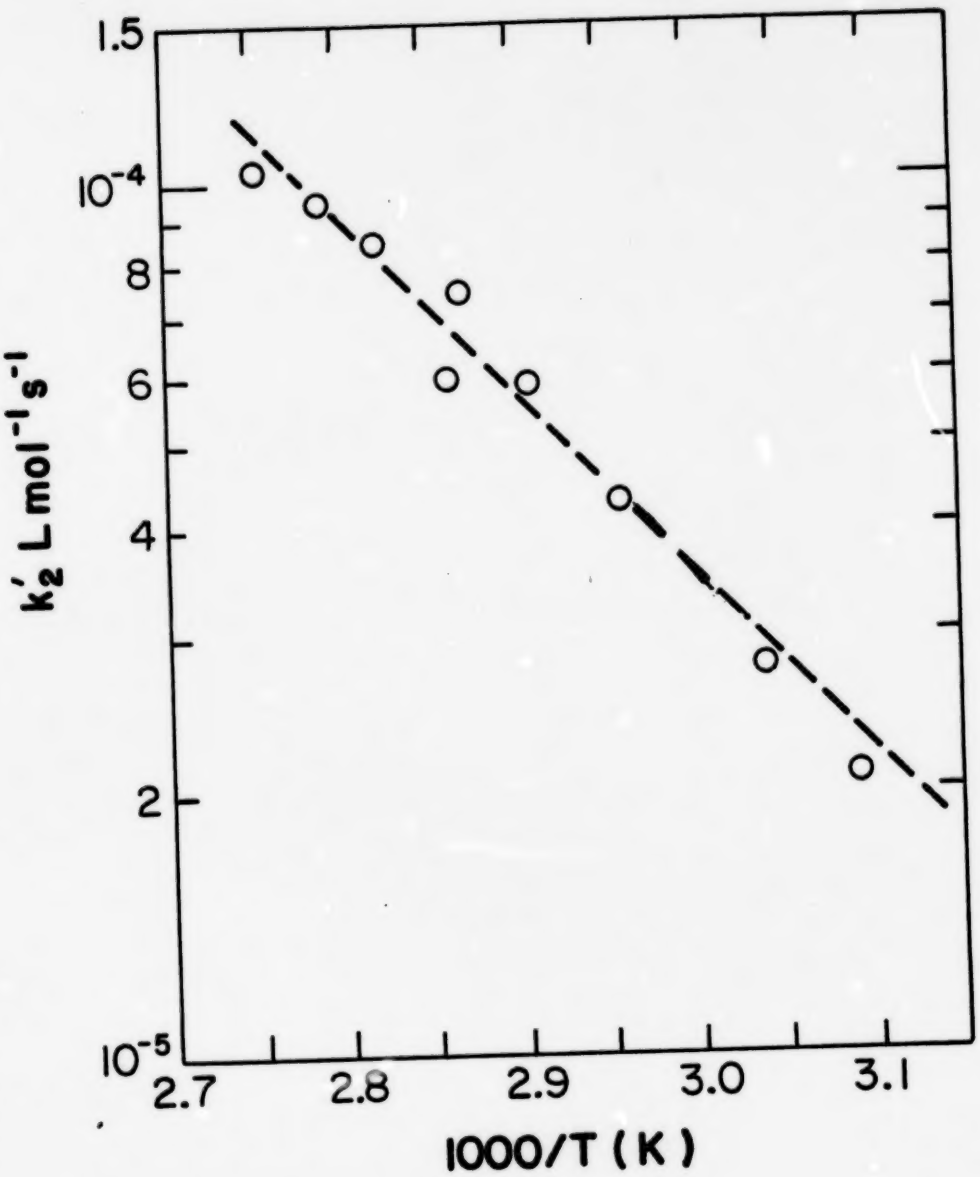

Fig. 17 - Arrhenius plot of the pseudo-second order rate constants presented in Table 3.

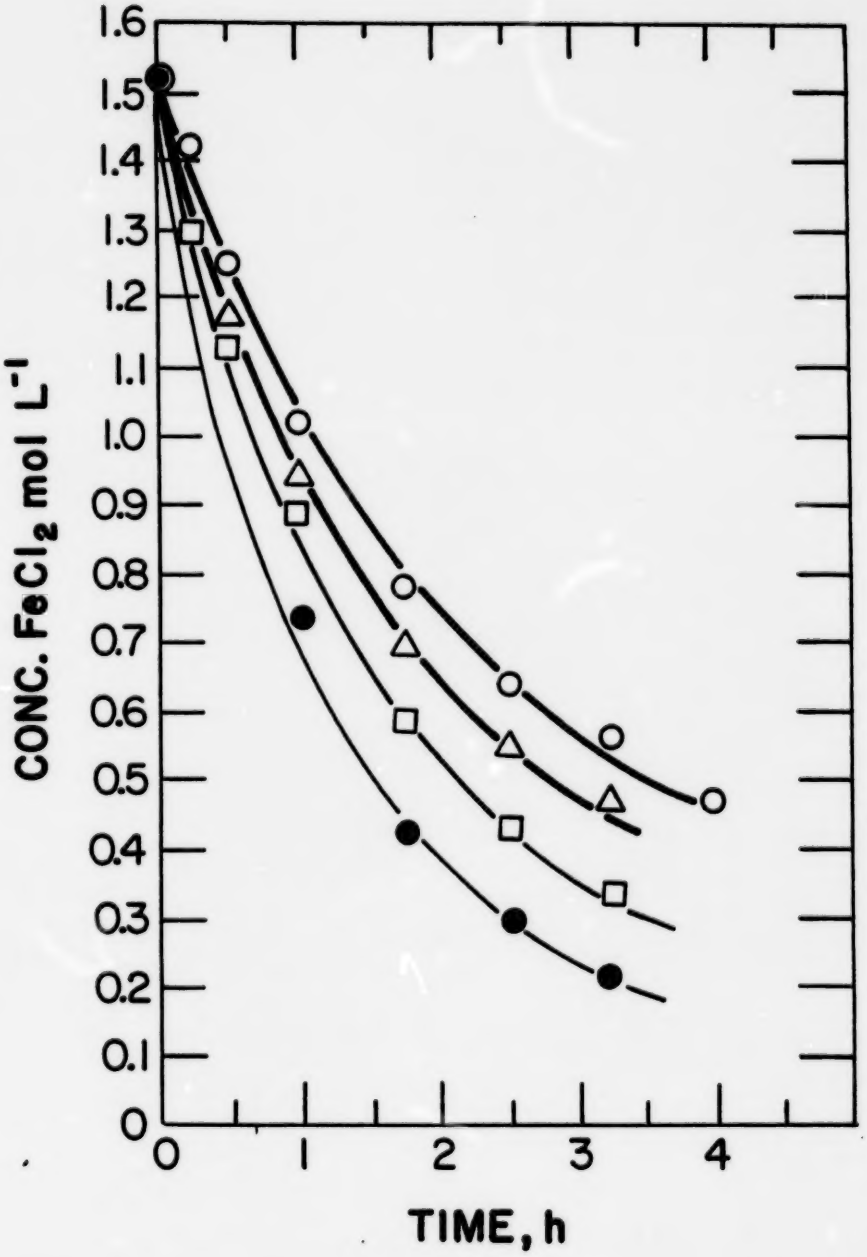

Fig. 18 - Oxidation curves illustrating the oxidation of 1.5 M $FeCl_2$ in 0.5 M HCl.

○ nil NaCl; △ 0.5 M NaCl; □ 2.0 M NaCl; ● 2.8 M NaCl.

Fig. 18.

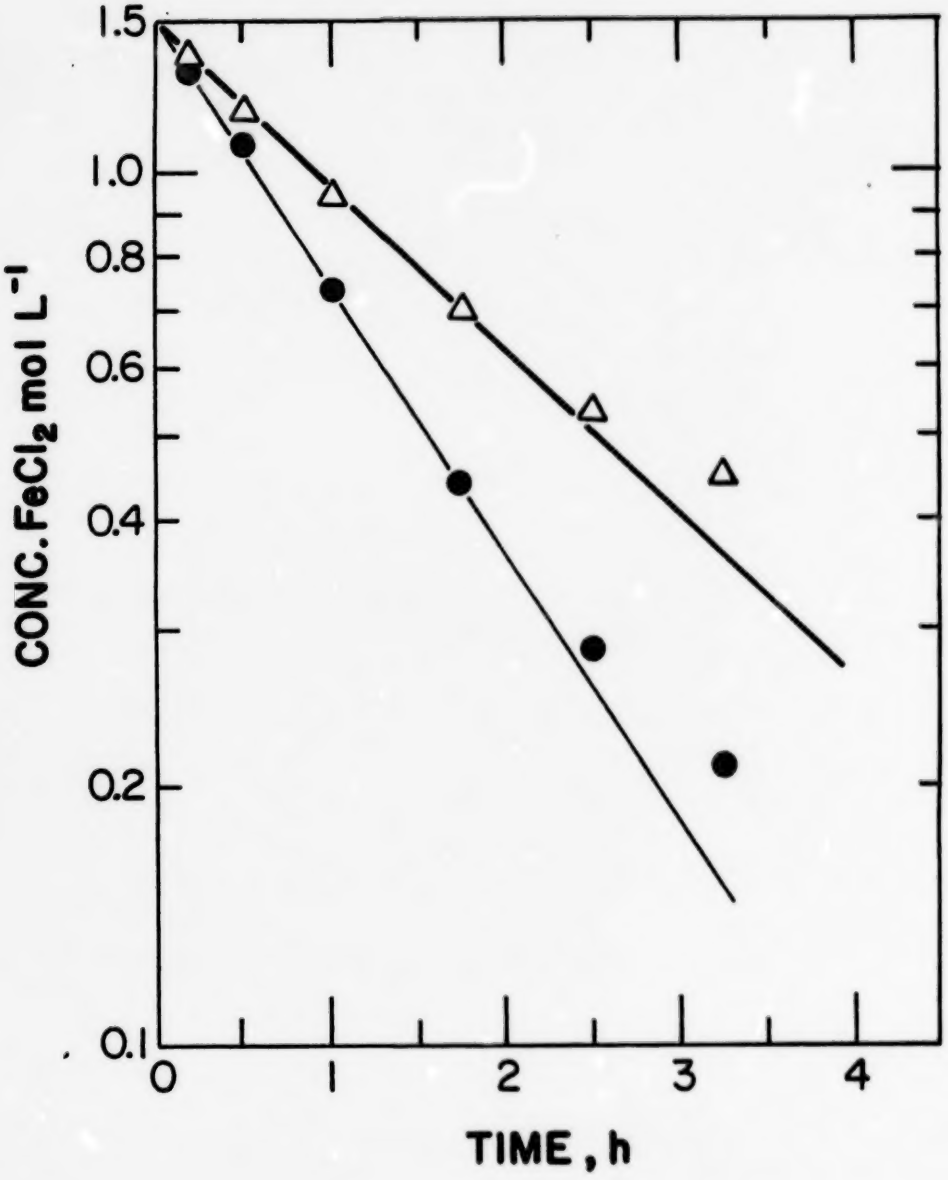

Fig. 19 - Semilogarithmic plots of the kinetic data of Figure 18.

Δ 0.5 M NaCl; ● 2.8 M NaCl

Fig. 19

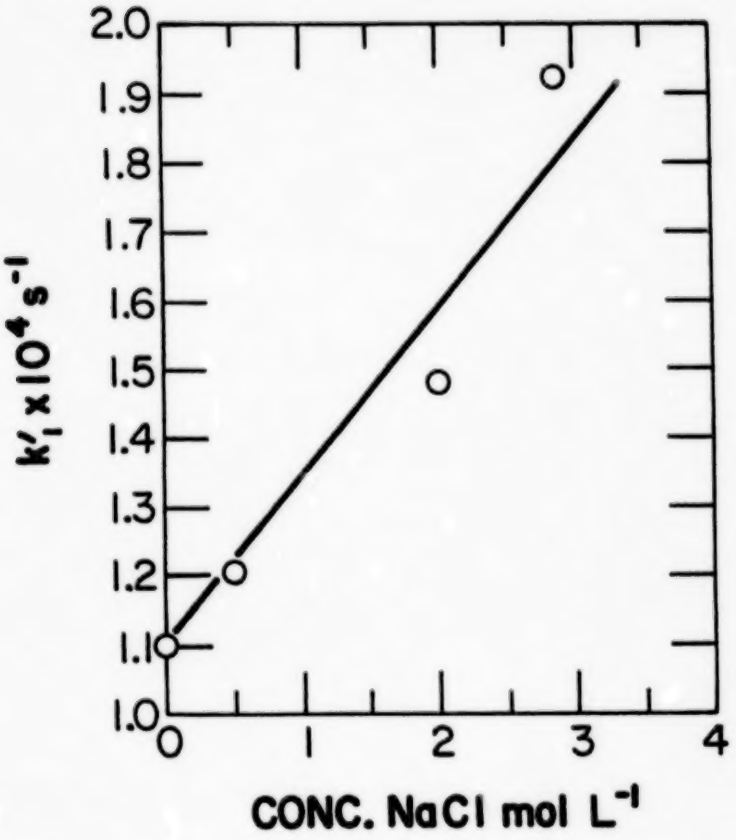

Fig. 20 - A plot of the pseudo-first order rate constant against the concentration of NaCl.